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**ELECTRONIC STRUCTURE AND MECHANICAL
PROPERTIES OF METALS AND INTERMETALLICS**

FINAL PROGRESS REPORT (3/2000 – 3/2004)

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SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

During the 2000-2004 grant period we have carried out first principles electronic structure calculations of the L1₂-type ordered nickel-based intermetallics, fcc metals, and carbon nanotubes, all exhibiting unique mechanical properties that make them attractive for aerospace and U.S. Army structural applications at elevated temperatures. This research work is supported by the US Army Grant (DAAD19-00-1-0049). The immediate motivation of this research work is the unusual mechanical properties of this class of intermetallics (high melting temperature, low density, good oxidation resistance, and *increase* of yield stress with *increasing* temperature in contrast to conventional compounds) and their importance in designing new ductile ordered superalloys and the need for a theoretical understanding at the atomistic level of the electronic and mechanical properties. The scientific personnel involved in the research work is listed in Sec. III. Eighteen publications resulted from this research work during the 2000-2004 period and are listed in the Publications section of the report (Sec. IV).

I. Aims

A major part of our effort focused on applying state-of-the-art first principles electronic structure calculations to study systematically:

1. The dislocation constriction and cross-slip in Aluminum and Silver;
2. The effect of sampling scheme of the misfit energy across the glide plane;
3. The Hydrogen-enhanced local plasticity in aluminum;
4. The correlation of the topology of the electronic charge density with the energetics and stability of planar faults in *fcc* metals;
5. The grain boundary sliding properties in aluminum and the effect of a vacancy on the grain boundary migration;
6. The effect of hydrogenation on the electronic structure of single-walled carbon nanotubes;
7. The electronic structure of metal/ceramic interfaces between Al₂O₃ and titanium overlayers;
8. The electronic structure calculations of H₂O adsorption on the Ni₃Al (001) surface,
9. The dislocation core properties of Cu-Al alloys.
10. Write a review article on "Multiscale Modeling"

These microscopic quantum mechanical calculations are based on the full-potential Linear-Muffin-Tin-Orbital (FPLMTO) method and the pseudopotential method and include structural relaxations. The *full potential* capability is *essential* when dealing with intermetallic compounds, which combine those characteristics common to covalently bound materials with metallic properties - a fairly uncommon combination. In contrast to atomistic simulations based on empirical potentials or the embedded-atom method involving the process of fitting parameters, first principles electronic structure calculations provide insight into the chemical bonding characteristics which ensue the cohesiveness of interatomic forces that control mechanical properties, and allow the possibility of not only studying "clean" intermetallics, but also intermetallics containing chemically different impurities.

II. Results/significance

1. Dislocation constriction and cross-slip in Aluminum and Silver: An ab initio Study

The cross-slip process by which a screw dislocation moves from one slip plane to another, plays an important role for plastic deformation in materials. For example, cross-slip is considered to be responsible for the onset of stage III in the stress-strain work-hardening curves. Furthermore, cross-slip can result in the formation of glide plane obstacles (sessile segments) in hcp metals and in L₁-, B₂- and L₁_o- based intermetallic alloys, responsible for the anomalous high-temperature yield stress peak. However, theoretical studies of alloying and impurity effects on dislocation cross slip have proved to be particularly difficult because one has to deal with both long-ranged elastic interactions (between dislocation segments) and short-ranged atomic interactions (due to the constriction process) that are inherent in a cross-slip process.

There are currently two theoretical approaches to study cross-slip. One is based on the line tension approximation which completely ignores atomic interactions. The other approach is direct atomistic simulations employing empirical potentials. Although the second approach is quite powerful in determining cross-slip transition paths and estimating the corresponding activation energy barriers, it is time-consuming and, more importantly, it critically depends on the accuracy and availability of the empirical potentials employed in the simulations. For example, reliable interatomic potentials usually are not available for multi-elements materials. As a consequence, the possible hardening mechanisms due to alloying for most materials are still uncertain, and the design of new materials based on favorable cross-slip properties lacks guidance. Thus, the understanding at an atomic level of the chemistry effect on the dislocation core properties and cross-slip mechanisms is of great importance in predicting and controlling plastic deformation in structural materials, since the deformation behavior is often associated with the presence of substitutional or interstitial alloying elements. *The ultimate goal of theoretical studies is then to use this information to help design through alloying new materials with desired mechanical properties in order to tailor the dislocation cross-slip behavior - in close collaboration with experimental efforts.*

In this work, we introduce a novel model based on the Peierls-Nabarro (P-N) framework which allows the study of dislocation cross-slip employing ab initio calculations. In fact, there has been a resurgence of interest recently in applying the simple and tractable P-N model to study dislocation core structure and mobility in conjunction with *ab initio* -surface calculations. *This approach represents a combination of an atomistic treatment of the interactions across the slip plane and an elastic treatment of the continua on either side of the slip plane. Therefore, this approach is particularly useful for studying the interaction of impurities with dislocations when empirical potentials are either not available or not reliable to deal with such multi-element systems. Furthermore, it allows to study general trends in dislocation core properties and to correlate them with specific features of the underlying electronic structure.* However, to date, all models based on the P-N framework are applicable only to a single slip plane while the important cross-slip process requires at least two active intersecting slip planes, i.e., the primary and cross-slip planes. In this work the semidiscrete variational P-N model is extended so as to take into account two intersecting slip planes. We have applied this new model to study the dislocation constriction and cross-slip process in two fcc metals, Al and Ag, exhibiting different deformation properties. We are particularly interested in the evolution of the dislocation core structure under external stress and the interplay between the applied stress and cross-slip process.

We find that the screw dislocation in Al can spontaneously spread into the cross-slip plane, while in Ag it dissociates into partials and can not cross-slip. We have also examined in detail the response of the dislocation core structure to an external Escaig stress and the effect of negative Escaig stress on the constriction of the Shockley partials. We find that we can not achieve 100% constriction for the case of straight partial dislocations considered in this work. By computing the dislocation core energy under stress we estimate the dislocation constriction energy for Al and Ag. The calculated values of the critical stress and the energy barrier for dislocation cross-slip demonstrate that dislocation cross-slip is much

easier in Al than in Ag. Since our *ab initio* based model is much more expedient than direct *ab initio* atomistic simulations, it can serve as a powerful and efficient tool for alloy design, where the goal is to select the ``right'' elements with the ``right'' alloy composition to tailor desired mechanical, and in particular, dislocation properties, such as cross-slip properties.

2. Effect of sampling scheme of the misfit energy across the glide plane

We have reexamined also two essential issues within the Peierls-Nabarro model which are critical in obtaining accurate values for the Peierls stress. The first issue is related to the sampling scheme of the misfit energy across the glide plane and the second one is the effect of relaxation on the Peierls stress. *We have shown that most of the current applications of the Peierls-Nabarro model do not treat properly the two issues and therefore are not able to predict reliable values for the Peierls stress.* The double counting scheme for the misfit energy at both sides of the glide plane was found to be physically more reasonable, and to predict more accurate values for the Peierls stress, especially for dislocations with equal spacing between alternating atomic rows. We have derived an analytical expression of the Peierls stress for dislocation in alternating-type lattices, which demonstrates for the first time the effect of atomic spacing (even versus uneven) on the Peierls stress. Finally, our results demonstrate the importance for allowing relaxation when a dislocation traverses the Peierls barrier, which in turn lowers the Peierls stress for narrow dislocations by an order of magnitude.

3. Hydrogen-enhanced local plasticity (HELP) in aluminum: an *ab initio* study

The mechanical properties of solids are not only a function of their intrinsic atomic structure, but also of the environment in which they exist. Small amount of impurity atoms in the environment can drastically change the response of a solid to external loading. Hydrogen embrittlement is one of most important and well-studied processes of environmental degradation of materials. After over a century of studies, the definitive mechanism of H embrittlement still remains unknown although significant progress has been made toward developing a detailed understanding of the problem. Three general mechanisms of H embrittlement have been proposed: (1) Formation of a hydride phase; (2) H-enhanced local plasticity; and (3) H-induced grain boundary weakening. The underlying atomic processes and the relative importance of the three mechanisms, however, remain uncertain and controversial.

In this work, we studied a key aspect of H embrittlement, referred to as H-enhanced local plasticity (HELP), which has attracted much attention recently. There seems to be overwhelming evidence that plasticity is a fundamental contributor to H embrittlement of virtually all susceptible metals and alloys, including Al, the model material we consider in this study. The most dramatic experimental observation is that H increases dislocation mobility significantly under constant stress. *This H-enhanced mobility is observed for screw, edge, and mixed dislocations. Other important experimental results include the observations of slip planarity, and strong binding between H and dislocation cores.* In contrast to the vast body of experimental evidence, theoretical studies of the HELP mechanism are scarce. *The purpose of our work is to provide a comprehensive understanding of the aforementioned experimental results based on an *ab initio* theoretical framework, which hopefully can set the stage for an atomistic theory of H embrittlement.*

We have used the recently developed Semidiscrete Variational Peierls-Nabarro (SVPN) model with *ab initio* determined -surfaces and elastic constants. We have previously shown that this approach can predict reliable dislocation core properties by comparing its predictions to direct atomistic simulations based on the same force law as that used for the -surface calculations. *The uniqueness of the approach when combined with *ab initio* calculations for the energetics is that it produces essentially an atomistic simulation for dislocation core properties without suffering from the uncertainties associated with empirical potentials.* Comparison of the -surface in the presence or absence of Hydrogen, we find an overall reduction in energy in the presence of H, indicating that dislocation can be emitted more easily from a crack tip when H is present. More importantly, we find that the Peierls stress, which is the minimum stress to move a stationary dislocation, is reduced by more than order of magnitude in the presence of H. Not only is our calculation the first successful attempt to explain HELP associated with individual dislocation behavior, it also invalidates the perception that the only plausible explanation of

HELP must be based on elastic interactions among dislocations and that the dislocation-lattice interaction is not important.

Other important experimental results that any theory of H embrittlement must explain are the observed H trapping in dislocation cores and the H-induced slip planarity. We find that there is a strong binding between H and dislocation cores and that the H is attracted (trapped) to dislocation cores to lower the core energies. Furthermore, the binding energy is found to increase with the amount of edge component. These results have significant consequences for the experimentally observed inhibition of cross slip and slip planarity in the presence of H. We find that H can stabilize the edge component of a mixed dislocation and inhibit the dislocation cross-slip process, leading to the observed slip planarity. *Thus, our results explain the experimentally observed restriction of the cross-slip process and slip planarity in the presence of H. Finally, based on the results of our calculations, we identify the process which could lead to H embrittlement. Namely, (a) H is attracted to crack tips; (b) H impurities at the crack tip facilitate dislocation generation and enhance mobility, which will lead to extensive plastic deformation in front of the crack, causing thinning and softening of the material ahead the crack tip; and (c) the thinning and softening processes, along with the localization of slip due to inhibition of cross slip, allow the crack to propagate at lower stress levels, prior to general yielding away from the crack tip.* Although our calculations concern Al, we believe that the results are also applicable to other metals.

4. Correlation of Topology of Charge Density with the Energy and Stability of Planar Faults in Metals

The competition between ductile and brittle behavior is of importance in the design of products using metallic components, for ductile failure occurs over many cycles of operation, whereas brittle failure often occurs suddenly with catastrophic results. An explanation for the susceptibility of a material to cleavage could be determined by a straightforward assessment of the relative strengths of bonds across the cleavage plane to those across slip plane. The purpose of this work was to investigate the correlation of the energetics associated with the shear deformation in fcc metals (Al and Ag) and the evolution of the topology of the electronic charge density. During the shear process where a bond is broken, the extra charge located in the metal bond being broken must be redistributed. The redistribution of this charge will depend on the local environment, which can either accommodate this charge in the existing unbroken bonds or not.

We have studied two prototypical ductile metals, Al and Ag, which have quite different deformation properties. The intrinsic stacking fault energy in aluminum (166 mJ/m^2) is about five times larger than that of silver (30 mJ/m^2). The value of the intrinsic stacking fault energy dictates the dissociation of full dislocations and the separation between the partials. The EAM potential, used very often to study mechanical properties in metals (crack propagation, etc.) underestimates the intrinsic stacking fault energy by a factor of two. This indicates the importance of using full potential electronic structure calculations (FPLMTO) which provide not only accurate energetics but also information on the topology of the charge density responsible for the rearrangement of bonds. The *ab initio* calculated intrinsic stacking fault energies are in excellent agreement with experiment. We find that the slip process occurs earlier (50% of the shear displacement) for Ag and later (63% of the shear displacement) for Al. The unstable stacking fault energy is 219 mJ/m^2 and 195 mJ/m^2 for Al and Ag, respectively.

We have calculated the evolution of the charge density in a plane perpendicular to the bond direction between a pair of A-C atoms across the shear (111) plane as the A-C bond forms, for both Al and Ag. At zero shear, the curvatures along and perpendicular to the bond direction of the breaking AC bond in Ag are about an order of magnitude larger than the corresponding ones in Al. On the other hand, at zero shear the curvatures for the forming bond are similar for both Al and Ag. During the shear process we find the following interesting and important results. Note, that at the position where the energy reaches its maximum value, at least one of the two curvatures perpendicular to the bond vanishes (signaling a topological instability). More specifically, for Ag both curvatures perpendicular to the bond vanish at the unstable stacking fault energy, whereas for Al only one goes to zero at the unstable stacking fault energy whereas the other vanishes very close to the intrinsic stacking fault energy. These results

indicate that the bond breaking and bond forming processes for Ag are accommodated with an *easier* redistribution of charge. In fact, the topology of the charge density for Ag at the intrinsic stacking fault energy is very similar to the unsheared bulk configuration. This explains the fact that the intrinsic stacking fault energy of Ag is five times smaller than that for Al. On the other hand, the charge density of Al for the intrinsic stacking fault configuration resembles that for the unstable stacking fault configuration and hence the corresponding energies are quite similar. The fact that the bonds of Ag respond to the shear strain in an electrophilic manner is closely related to the fact that Ag has only s orbitals while Al has both 3s and 3p contributing to the bonding (the p orbitals of Al are more directional).

In summary, we have employed *ab initio* calculations to study the energetics and the evolution of the charge density with shear in three fcc metals, Al, Ag, and Ir, exhibiting different deformation properties. The charge redistribution accompanying this process is described by the change in character of specific charge density critical points, with bond breaking associated with a transformation of a bond critical point to cage critical point, while the bond formation is associated with the reverse. For all three materials, χ_{hh} vanishes near the unstable stacking fault configuration. We find that the symmetry or asymmetry of the charge redistribution, as measured by χ_{hh}/χ_{vv} may be an important factor determining the stacking fault energies in fcc metals.

5. Grain boundary sliding in Aluminum

It is well established that grain boundaries play an important role in the behavior of materials, particularly in its inelastic response as well as fast self-diffusion mechanism along the plane of the interface. The most pronounced structural feature of a grain boundary is the atomic-level disorder near the interface even at zero temperature. The fact that structural properties at or near the interface can differ dramatically from those of the surrounded bulk material determines its inelastic response. Rigid body translation parallel to the interface strongly affects the atomic structure along the interface and plays an important role in the deformation process providing plastic shear displacements, i.e. superplastic flow. Two principal mechanisms of plastic flow at intermediate-to-high temperatures are grain boundary sliding and diffusional flow. Computer simulations offer the unique ability to examine the details of the grain boundary sliding under the application of external stress.

Finite-temperature Monte Carlo simulations

While *ab initio* electronic structure calculations provide accurate structural information and energetics, they are limited to a small ensemble of atoms. combined with the EAM potential have been employed to investigate the microscopic process of the 5 tilt grain boundary sliding in aluminum. We have studied the atomic structures and the grain boundary sliding/migration energy profile at elevated temperatures in the absence or presence of vacancies. The annealing temperature is found to play an important role in determining the grain boundary energetics and mobility. Contrary to *static* simulations, the *simulated annealing* (SA) produces new lower energy states of the complex and low-symmetry grain boundary structure. *The vacancy formation energy at the first layer from the interface is found to be significantly lower than that at the other layers and the bulk.* On the other hand, the vacancy at the interface has significantly higher formation energy compared to bulk, in very good agreement with recent *ab initio* electronic structure calculations. For both *static* and SA simulations, the grain boundary sliding energy profile is smooth, exhibiting several energy peaks and valleys, where the latter is associated with grain boundary migration. The SA scheme reduces the grain boundary sliding/migration energy barrier by about a factor of three and increases the rate of migrations. The distribution of atomic energies helps identify the atoms that play a key role in the grain boundary sliding and migration. The grain boundary sliding energy profile in the presence of a vacancy placed at the first layer is very similar to that of the clean boundary, while the vacancy at the interface increases the grain boundary energy and leads to no migration. Analysis of the energies of the atoms in the grain boundary region provides insight into which atoms play an important role for the grain boundary migration.

Ab initio Electronic Structure Calculations

We have applied *ab initio* electronic structure to investigate the electronic origin of the effect of a vacancy on the grain boundary sliding of the 5 tilt grain boundary in Al. In order to gain a full understanding of the interaction of the vacancy with the grain boundary, we have placed the vacancy at various possible atomic sites. Our results show that the vacancy formation energy depends on the local atomic environment of the vacancy. More specifically, we find that the vacancy formation energy is higher than its bulk value (0.1 eV) when the vacancy is placed at the grain boundary plane, and is much lower (0.23 eV) than the bulk value when the vacancy is at the first layer to the boundary. These results indicate that the grain boundary does not always act as a sink of vacancies. Rather, vacancies migrate selectively to planes adjacent to the boundary. Another important finding is that the atomic relaxation induced by the vacancy is larger than that due to the grain boundary (GB expansion). We have calculated also the energy profile during sliding in the presence of a vacancy. Interestingly, we find that the vacancy increases the sliding energy barrier by a factor of about three compared to that for the pure GB, and it eliminates completely grain boundary migration. The inhibition of one mode of GB motion and GB migration by a single vacancy, is similar to the dragging effect for dislocation motion induced by a point defect atmosphere. These results suggest that creation of vacancies at GB may improve the high temperature stability of polycrystalline materials, just as the common practice of solute strengthening in alloys.

6. Effect of hydrogenation on the electronic structure of single-walled carbon nanotubes

Carbon nanotubes reveal diverse physical properties depending on their diameter and chirality. The large empty space, particularly inside the single-walled nanotubes, their chemical stability and low mass density, opens new possibilities for applications in novel nanoscale materials and device structures. In particular, there has been considerable interest recently in evaluating the capability of carbon nanotubes as a hydrogen-storage material for clean energy sources. Hydrogen could be stored in bundles of the single-walled nanotubes up to 5-10 wt. % at pressures less than 1 bar near room temperature. The mechanism, is for the most part, attributed to H₂ physisorption both inside the tubes and in the interstitial regions between nanotubes, in agreement with several theoretical studies based on classical molecular dynamics and density functional theory calculations of H₂ on a graphene layer.

Recently, Smalley and coworkers recently discovered an interesting phenomenon: under hydrogen atmosphere, single wall armchair nanotubes annealed up to 1500C coalesce with neighbors, resulting in nanotubes with twice and occasionally three times the diameter of the original nanotube. Based on these results, these authors proposed a hydrogen-activated coalescence mechanism, in which gas-phase H-atoms attack the side of neighboring nanotubes, breaking the C-C bonds, producing defective sites on adjacent nanotubes. Once these adjacent defects have formed, there will be a strong thermodynamic driving force, resulting from the reduced strain energy of larger diameter tubes, for the two neighboring tubes to join together. Coalescence of clean single-walled nanotubes has also been observed under electron irradiation conditions at elevated temperatures.

In this work, we have carried out the first *ab initio* study of chemisorption of *atomic* hydrogen on the (5,5), (6,6), (7,7), (8,8), (9,9), (10,10), and (11,11) armchair tubes and for the (7,0), (9,0) and (10,0) zigzag nanotubes. This hydrogenation can occur during the electrochemical storage process, where one first has to break H₂ molecules into hydrogen atoms, by using a metal catalyst or electrochemical techniques. The purpose of this work is to clarify the underlying electronic structure responsible for the adsorption properties of a single and two hydrogen atoms placed both in the exterior and interior of the nanotube. *Our calculations provide for the first time direct evidence of the selective hydrogen-induced unzipping of the nanotube through the concerted formation of two C-H bonds, which explains the hydrogen-activated coalescence phenomena discovered recently by Smalley and coworkers.*

We have carried out a systematic first-principles study of the H-induced unzipping phenomenon (scission of a row of C-C bonds along the tube axis) of single-walled armchair and zigzag nanotubes. We select the (6,6) armchair nanotube as a representative case to demonstrate the generic unzipping mechanism. We find that a single H atom can weaken the C-C bond. We predict that two rows of H

atoms chemisorbed on selective sites *exterior* to the smaller armchair nanotubes can break the nearest-neighbor C-C bonds of the nanotubes through the concerted formation of C-H bonds, leading to the unzipping of the nanotube wall. For all the nanotubes under study, we find that there is no H-induced unzipping when H atoms are chemisorbed at the interior of the tubes. Overall, the internal surface of the nanotube is found to be less reactive than the external surface, in agreement with the general consensus.

In order to clarify the effect of the nanotube radius on the propensity of unzipping, we have carried out similar calculations for the (5,5), (7,7), (8,8), (9,9), (10,10) and (11,11) armchair tubes. In all cases the two H atoms are chemisorbed outside the tube on two nearest-neighbor C atoms at the same layer, i.e., same configuration used for the (6,6) tube. We find that the four smaller tubes all exhibit the same H-induced unzipping, while the larger (10,10) and (11,11) tubes remain intact, i.e., no C-C bond is broken. These results are consistent with the fact that (*i*) both bond lengths, of the bonds perpendicular to the tube axis and of the other inequivalent (zigzag) bonds, increase with decreasing tube radius; and (*ii*) the *difference* between them also increases with decreasing radius, with the former being longer and hence weaker. Therefore, the nanotubes with smaller radius are under larger strain and are more susceptible to the H-induced unzipping. In order to have a more complete picture of the unzipping phenomenon, we have performed additional calculations for the (7,0), (9,0) and (10,0) zigzag tubes with two H atoms chemisorbed exterior to the tubes. In the zigzag tubes there are two inequivalent nearest-neighbor C-C bonds: one parallel and the other zigzag to the tube axis. Since none of these bonds in a zigzag tube are strained as much as those on the same layer in an armchair tube, one would expect that the zigzag tubes are more stable against the H-induced unzipping. Indeed, our calculations confirm that the zigzag tubes are stable and that their C-C bonds remain intact. Thus, our results indicate that the C-C bonds that are perpendicular (parallel) to the tube axis are the most (least) strained, and that the strain of the zigzag C-C bonds lies in between the two extreme cases. This general rule is also consistent with the finding that the C-C bonds at two different layers of the (6,6) tube are stronger than those at the same layer. Finally, our results suggest that the metallic/semi-conducting nature of a nanotube *is not* the deciding factor for the unzipping phenomenon. Some of the metallic tubes, such as the smaller armchair tubes can be unzipped, while the other metallic tubes, such as the larger armchair tubes and the (9,0) zigzag tube can not be unzipped. More calculations are needed to ascertain if all semi-conducting tubes are stable against unzipping. Also, since our *ab initio* calculations are carried out at zero-temperature, one should be cautious to compare the theoretical predictions with the finite-temperature experimental results.

In conclusion, we have studied the hydrogenation of a metallic single-walled (6,6) armchair nanotube. We find that a single hydrogen binds strongly to the nanotube through sp^3 bonding, with the binding energy being larger in the exterior of the tube. The observed change of the local DOS via hydrogenation can be used for tailoring the local electronic properties of these structures along the axis of the tube. We predict that a pair of hydrogen atoms chemisorbed on selective sites exterior to the nanotube catalyzes the breaking of the nearest-neighbor C-C bond through the concerted formation of two C-H bonds, leading to the unzipping and scission of the nanotube. This hydrogen-induced zipper-like mechanism lends strong support to the recent experimental observations of Smalley and coworkers for the coalescence of single-walled nanotubes in the presence of atomic hydrogen. On the other hand, the C-C bond does not break when hydrogen is adsorbed in the interior of the wall.

7. Electronic structure of Ti/Al₂O₃ interfaces

Metal/metal oxide interfaces are crucial to electronics devices, and aluminum (Al₂O₃) and titanium (TiO₂) oxides play pivotal roles. The Ti:sapphire interface at low Ti coverage has notable applications in high power laser and optoelectronics waveguide technologies. More generally, Ti/Al oxide interfaces occur in several applications. These include, for example, Ti/Al alloys for aerospace/automotive applications, when an Al₂O₃ coat evolves into Al₂O₃+TiO₂, or nano-layered sandwich structures, such as Cu, Ag/Ti/Al₂O₃, where Ti prewetting improves Cu and Ag adhesion.

While an extensive literature exists in general for clean oxide surfaces and metal- or oxide-oxide interfaces, much less effort has been devoted to understanding the specific Ti:sapphire interface. Although crucial to the technological applications mentioned above, many aspects of such interface are currently uncertain. Furthermore, the current microscopic understanding of the Ti:sapphire interface drives exclusively from experiment, with temperatures in these studies varying from 300K to above 1100K. In some cases, experimental evidence is inconclusive: for example, RHEED and ion scattering results for low-dosage, shallow-implant Ti, indicate that Ti is in the surface layer atop the (subsurface) Al atoms, even though the actual site preference of the substitution is uncertain. Also, this leads to commensurate growth of crystalline Ti. Moreover, XPS and Auger data show clearly that at elevated temperatures the metallic Al 2p signal is present and the shape of the valence bands, which have primarily oxygen character, are broadened. Furthermore, the Ti 2p signal is shifted. All of this is consistent with the formation of an oxidized Ti layer and concomitant partial Al_2O_3 reduction.

In this work we have carried out the first *ab initio* density functional calculations to elucidate the nature of the Ti:sapphire interface. We find that: (i) Substitutional Ti prefers to replace the terminating Al rather than the subsurface Al and, additionally, little deformation of the surface occurs in the latter case; (ii) a single Ti adatom on sapphire displaces the terminating Al rather than adsorbing atop the surface; and (iii) a mixed Ti_2Al adlayer on a Ti-terminated oxide surface is preferred over a sharp $\text{Ti}_3:\text{Al}_2\text{O}_3$ interface. These results indicate that the Al-terminated surface is unstable to Ti adsorption, and predict a mixed Al/Ti interfacial layer.

Our study is the first *ab initio* description of the $\text{Ti}_x\text{Al}_2\text{O}_3$ interface and provides a theoretical rationalization, consistent with available experiments, of many aspects of the interfacial behavior. These are the surface rigidity of sapphire for dilute shallow Ti impurities; the Ti preference for surface rather than subsurface replacement of Al; the instability of the Al-terminated sapphire surface in the presence of Ti; and the consequent formation of a mixed Al/Ti layer at the onset of interface formation. These results should be germane to other $\text{Ti}_x\text{Al}_y\text{O}_z$ phases of Ti/Al-based technological materials, and informative to the adsorption of other metals on the Al_2O_3 surface. One publication resulted from this work.

8. Electronic and adsorption properties of H_2O on Ni_3Al (001) surface

Ni_3Al is a member of a class of Ni based intermetallics (Ni_3X , X=Al, Ga, Si, Ge), which are potential candidates for a wide variety of structural applications at elevated temperatures. A unique feature of this class of materials is the increase of yield stress with increasing temperature, in contrast to fcc metals. Other properties of central interest include a high melting temperature (1390°C) and the ability to resist oxidation. However, one of the serious limitations of Ni_3Al in practical applications is the so-called environmental embrittlement. While single Ni_3Al crystals are ductile, polycrystalline samples fail intergranularly due to segregation of harmful impurities at the grain boundaries.¹

Experimental studies¹⁻³ of a large number of ordered intermetallics demonstrated that the ductility is a strong function of test environment, namely the poor ductility in air is due to moisture-induced embrittlement. The proposed mechanism for this moisture-induced embrittlement is that water reacts with fresh metal surfaces exposed during mechanical testing to produce atomic hydrogen that penetrates into crack tips and causes embrittlement.⁴ The reaction associated with this phenomenon is: $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}$. It appears that the dissociation of water is structure-sensitive and that Al is the active species in controlling the dissociation of water on Ni_3Al surfaces.⁴

The interaction of H_2O with metal surfaces is of fundamental importance in many areas of research ranging from heterogenous catalysis, environmental protection, and corrosion to name the few. However, our atomic level understanding of H_2O adsorption systems remains unclear and basic questions on the binding site and orientation of H_2O monomers on metals and intermetallics surfaces remain unanswered. Experimental characterization of H_2O monomer adsorption is difficult, complicated by facile H_2O cluster formation. Cluster formation is problematic because it masks the true

H_2O -metal interaction, making it difficult to make any definitive statements about H_2O -metal bonding.⁵ In order to minimize cluster formation, it is necessary to work with low H_2O coverage at low temperatures ($<< 100\text{K}$). To date, it has not been possible with STM to resolve the internal structure of adsorbed H_2O molecules, nor has it been possible to determine the orientation of the H_2O molecule with respect to the surface normal.

The purpose of this study was to carry out *initio* electronic structure calculations of the water monomer adsorption on the (001) surface of Ni_3Al . One of the important issues addressed is the preferred orientation of H_2O on the surface because it will affect how H_2O responds to an applied electrochemical field, how H_2O dissociates, and the stability and structure of H_2O clusters that may form. Generally, it has been assumed that H_2O adsorbs “upright” with the O end down and the OH bonds pointing away from the surface, since this orientation maximizes the adsorbate-dipole substrate-image dipole interactions.⁶⁻⁷

Since a manuscript describing the results of this work is currently under preparation, we give here a more detailed accounting of the results. Total energy calculations within density functional theory (DFT) framework were performed using the pseudopotential method.

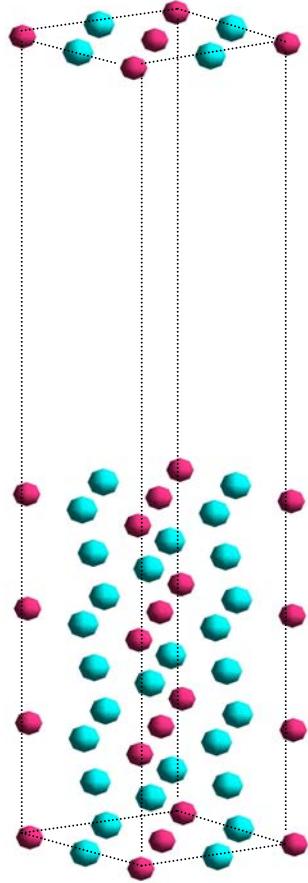


FIG. 1. 7-layer slab of the mixed (50% Al and 50% Ni) $\text{Ni}_3\text{Al}(001)$ surface. Red circles are aluminum and green circles are nickel.

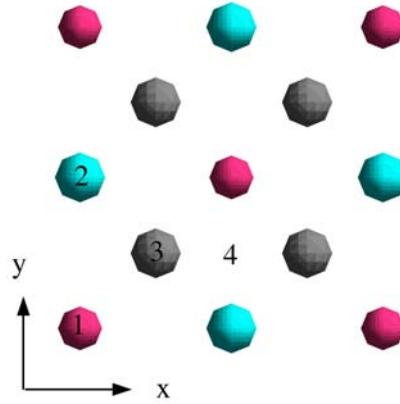


FIG. 2. Top view of the (001) surface indicating the four different adsorption sites (denoted by 1-4) for the H_2O molecule. Gray circles represent the Ni atoms in the subsurface.

The intermetallic (001) surface, shown in Fig. 1, was modeled by a periodic array of seven layer slabs, separated by a vacuum region equivalent to six layers. We have considered the mixed layer surface containing both Al and Ni atoms (50% each), since both our *ab initio* results and the low-energy electron diffraction (LEED) analysis of the clean surface, find that the mixed terminated surface is the most stable surface. A $p(2\times 2)$ unit cell was employed corresponding to 1/4 coverage of H_2O molecule which was placed on one side of the slab. We have considered four different adsorption sites shown in

Fig. 2: (1) H₂O atop of Al; (2) H₂O atop of Ni; (3) H₂O between Al; and (4) H₂O between Al and Ni. Structure optimizations were performed for a variety of initial orientations of the H₂O molecule. These included configurations in which H₂O was initially placed in the surface normal with the H atoms either pointing away from the surface (upright H₂O) or towards the surface as well as structures in which H₂O was initially parallel to the surface. The adsorption energies of water for the various adsorption sites are listed in Table I. Also listed in this table are the optimized structural parameters, including the O-H bond length and the HOH angle of the.

TABLE I. Adsorption energies and optimized structural parameters for each adsorption configuration. The adsorption energy, $E_{\text{ads}} = E(\text{Pure} + \text{H}_2\text{O}) - E(\text{Pure}) - E(\text{H}_2\text{O})$. Distances are in Å.

Configuration	E_{bind} (eV)	λz of O above surface	Distance from O to closest atom	O-H Length	HOH (°)
Isolated H ₂ O	-	-		0.973	105.483
Pure Relaxed	-	-		-	-
H ₂ O on Al	-0.180	2.134	2.144	0.985	107.332
H ₂ O on Ni	-0.247	2.243	2.251	0.978	106.039
H ₂ O between Al	0.057	2.915	3.428	0.975	105.936
H ₂ O between Al and Ni	-0.213	2.083	2.112	0.985	106.617
				0.994	

From this extensive set of DFT calculations we find: (i) the favorite adsorption site for H₂O is atop on the Ni atom; (ii) the energy barrier between the Ni and Al atop adsorption sites is 0.07 eV; and (iii) **at the Ni adsorption site H₂O lies nearly parallel to the surface**. More specifically, the tilt angle between the molecular plane and the horizontal is (1) 29.68° for H₂O atop Al; (2) 23.52° for H₂O atop Ni; (3) 89.16° for H₂O between Al atoms; and (4) 21.65° for H₂O between Al and Ni atoms. The fact that in the third configuration the angle is practically 90° is consistent with the fact that the molecule does not bind at that site (Table I). Similar tilt angles have been found recently for H₂O on various closed-packed transition metal surfaces⁸. From Table I several other interesting features of H₂O adsorption are revealed. First, H₂O deforms little upon adsorption: the O-H bonds are slightly elongated from a calculated gas phase of 0.97 Å to 0.97-0.98 Å; and the HOH angle is expanded by no more than 2° from a calculated gas phase value of 105°. Thus, our zero-temperature calculations indicate no dissociation which is agreement with low-temperature experiments. However, at higher temperature experiment suggest dissociation. Secondly, H₂O is laterally displaced from the precise atop site by about 0.3 Å and the potential energy surface for diffusion in the vicinity of the atop site is quite smooth, suggesting a stability of the molecule. The charge density contour plot for H₂O adsorption atop the Ni site is shown in Fig. 3. We find that there is a strong bond between the molecule and the Ni atom on the surface, consistent with the large adsorption energy in Table I.

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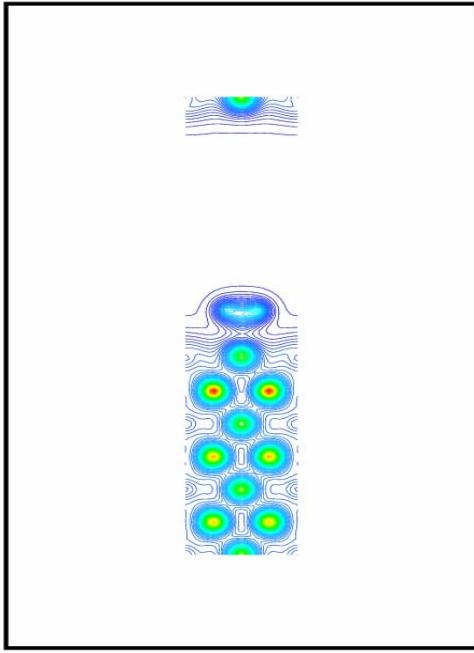


FIG. 3. Charge density contour plot for H_2O atop on Ni. The highest charge density is $2.73 \text{ e}/(\text{au})^3$.

9. Dislocation core properties of Cu-Al alloys

The strengthening of alloys relative to pure metals has been a subject of technological and scientific interest for centuries. Al-Cu alloys are the oldest in which age hardening has been understood to arise from solute precipitation. In age-hardened solid solution alloys small amounts of solute element (e.g. Cu) are added to the pure metal (e.g. Al) at high temperatures (where there is solubility) and the alloy is quenched down in temperature. With time the supersaturated solute atoms begin to precipitate. The aged alloy becomes stronger because dislocation motion through the crystal is impeded by the precipitate itself and by the elastic strain field surrounding the precipitate. These crystallographically coherent precipitates (i.e. without dislocations between the precipitates and the matrix) are collectively known as Guinier-Preston (GP) zones.^{1,2}

The GP zones are metastable phases, with a long relaxation time. In the Al-Cu system the Cu atoms coherently precipitate in the $\{100\}$ planes of the Al matrix. The shape and size of the precipitates has been a subject of long experimental and theoretical study. The coherent precipitation sequence was determined in the 50's as solid solution GP1 GP2. There has been some controversy as to what the structure of the GP zones is, but the following is usually accepted: GP1 is a single, almost pure, (100) Cu layer formed in the initial stages of precipitation; GP2 is primarily (but not only) an ordered platelet of two Cu $\{100\}$ planes separated by three $\{100\}$ planes of Al. Such a an ordered structure for GP2 has been inferred both from superlattice reflections in X-ray measurements,² and from first-principles thermodynamic calculations.³ While the Al_3Cu_1 was found to be the most stable, the Al_1Cu_1 ($\text{L}1_0$) ordered structure is very close in energy. In this work we have use the latter structure to model the GP zone since it involves smaller supercells and hence is computationally less expensive.

While the continuum elasticity theory describes well the long-range elastic strain of a dislocation for length scales beyond a few lattice spacings, it breaks down near the singularity in the region known as the dislocation core. Two types of theoretical approaches have been employed to study the core properties of dislocations. The first type is based on direct atomistic simulations using either empirical potentials or first-principles calculations. Empirical potentials may not be reliable in describing the core properties, while first-principles electronic structure calculations, although more accurate, are computationally too expensive for studies of dislocation properties. An alternative approach to study the dislocation core and cross slip properties is based on the Peierls framework with *ab initio* calculations

for the relevant energetics. *This approach is particularly useful for studying the interactions of impurities with dislocations, when empirical potentials are either not available or not reliable to deal with such multi-element systems.*

We have used the recently developed Semidiscrete Variational Peierls-Nabarro (SVPN) model with ab initio determined -surfaces and elastic constants. We have previously shown⁴⁻⁶ that this approach can predict reliable dislocation core properties by comparing its predictions to direct atomistic simulations based on the same force law as that used for the -surface calculations. *The uniqueness of the approach when combined with ab initio calculations for the energetics is that it produces essentially an atomistic simulation for dislocation core properties without suffering from the uncertainties associated with empirical potentials.*

To simulate the block shearing process, we employ a supercell consisting of six atomic layers in the <111> direction. We have considered two different cases of alloying: In the first case, which we will refer to as Al-Cu(a), we substitute one Al atom with a Cu atom on the shear layer, i.e. the shear plane consists of one Cu atom and three Al atoms with all other layers being pure Al. In the second case, which we will refer to as Al-Cu(b), each (111) layer consists of interchanging aluminum and copper chains along the <112> direction. The second case corresponds to the L1₀ ordered intermetallic with alternating Al and Cu (001) planes. The calculations were performed at the theoretically equilibrium lattice constant $a=4.0$ Å of pure Al, since the content of Cu in the alloys under study is about 1-2% and the Cu precipitates in the Al matrix are coherent. The generalized stacking fault energy (GSF) (surface) for both the Al-Cu(a) and Al-Cu(b) cases is shown in Fig. 4. For Al-Cu(a) the intrinsic stacking fault (ISF) energy is reduced to 0.122J/m² from 0.164J/m² for pure Al. The unstable-stacking energy is also reduced slightly from 0.224J/m² for pure Al to 0.175J/m². For Al-Cu(b) the GSF energy surface changes dramatically compared to that of pure Al. The ISF energy vanishes along [112] and in fact becomes negative -0.102J/m² along the [121] direction. The average of the two values compares well with the value of about -0.050J/m² for the 50 at.% random Al-Cu alloy.⁷

Finally, we discuss the results of the Peierls stress, which is a measure of the mobility of the dislocation (softening or hardening effect). For Al-Cu(a) the core energy for all four dislocations is higher than that for the pure Al case. We find that the Peierls stress for the screw, 30 , 60 dislocations is lower than for the pure Al case. On the other hand, the Peierls stress for the edge dislocation is an order of magnitude higher than that for the pure Al, which is probably due to the fact that the edge dislocation dissociates into partials for Al-Cu(a). In sharp contrast, all four dislocations for the Al-Cu(b) system have lower core energies than for Al-Cu(a), and the Peierls stress of all is an order of *magnitude higher* than that for Al-Cu(a), suggesting a strengthening mechanism.

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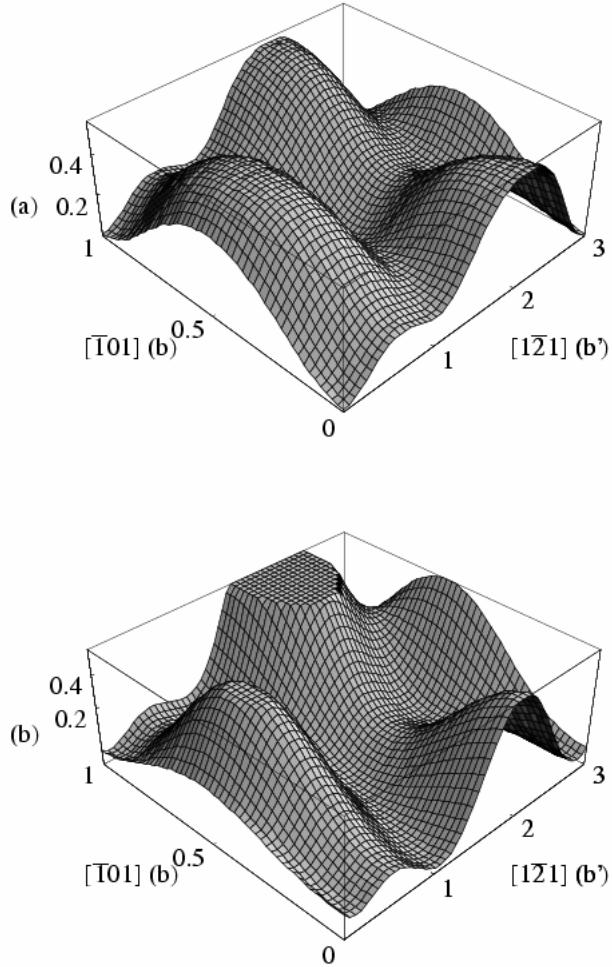


FIG. 4. The generalized stacking fault energy (GSF) (surface) for both the Al-Cu(a) and Al-Cu(b) cases.

10. Review article on “Multiscale modeling of nanomechanics and micromechanics”

In collaboration with Profs. Nasr Ghoniem (UCLA), Esteban Busso (Imperial College, UK) and Hanchen Huang (Rensselaer Polytechnic Institute) we wrote and published a review article entitled on “*Multiscale modeling of nanomechanics and micromechanics: an overview*”. The article is a review of recent advances in analytical and computational modeling frameworks to describe the mechanics of materials on scales ranging from the atomistic, through the microstructure or transitional, and up to the continuum. The role played by dislocation dynamics and statistical mechanics methods in understanding microstructure self-organization, heterogenous plastic deformation, materials instabilities and failure phenomena is also discussed.

III. Scientific Personnel

The following scientific personnel was involved in the research program during the 2001-2002 grant period and was supported by the US Army grant award: Prof. Nicholas Kioussis (PI), Drs. Gang Lu and A. Coho, (Post doctoral fellows); and Mr. Henry Scudder and Ms. M. Tovar (graduate students).

IV. Publications

1. *Generalized-stacking-fault energy surface and dislocation properties of aluminum*, G. Lu, N. Kioussis, V. Bulatov, and E. Kaxiras, *Phy. Rev. B* **62**, 3099 (2000).
2. *The Peierls-Nabarro model revisited*, G. Lu, N. Kioussis, V. Bulatov, and E. Kaxiras, *Phil. Mag. Lett.* **80**, 675 (2000).
3. *Tight-binding study of stacking faults and the Rice criterion of ductility in the fcc metals*, M. Mehl, D. Papaconstantopoulos, N. Kioussis, and M. Herbranson, *Phys. Rev. B* **61**, 4894 (2000).
4. *Dislocation core properties of aluminum: A first principles study*, G. Lu, N. Kioussis, V. Bulatov, and E. Kaxiras, *Mater. Scien. and Engin. A* **309-310**, 142 (2001).
5. *Effect of Hydrogen on Grain-Boundary Embrittlement: An ab initio study*, N. Kioussis, G. Lu, R. Wu, and M. Ciftan, in *Condensed Matter Theories*, eds. G. S. Anagnostatos, R.F. Bishop, K.A. Gernoth, J. Ginis, and A. Theofilou, **15**, 313 (Nova Science Publishers, 2000).
6. *Grain boundary sliding and migration: Effect of temperature and vacancy*, P. Ballo, N. Kioussis and G. Lu, *Phys. Rev. B* **64**, 024104 (2001).
7. *Interaction of vacancies with a grain boundary in aluminum*, G. Lu and N. Kioussis, *Phys. Rev. B* **64**, 024101 (2001).
8. *Hydrogen-enhanced local plasticity in aluminum: an ab initio study*, G. Lu, N. Kioussis and E. Kaxiras, *Phys. Rev. Lett.* **87**, 095501 (2001).
9. *Topology of Electronic Charge Density and Energetics of Planar Faults in fcc Metals*, N. Kioussis, M. Herbranson, and M. Eberhart, *Phys. Rev. Lett.* **88**, 125501 (2002).
10. *Layer intermixing during metal/metal oxide adsorption: Ti/sapphire (0001)*, C. Verdozzi, P. A. Schultz, R. Wu, A.H. Edwards, and N. Kioussis, *Phys. Rev. B* **66**, 125408 (2002).
11. *Dislocation constriction and cross-slip in Al and Ag: an ab initio study*, G. Lu, V. Bulatov, and N. Kioussis, *Phys. Rev. B* **66**, 144103 (2002).
12. *Multiscale Modeling of Nano- and Micro-Mechanics: An Overview*, Nasr M. Ghoniem, Hanchen Huang, Esteban Busso, and Nicholas Kioussis, *Phil. Mag. A* **83**, 3475 (2003).
13. *Hydrogen-induced unzipping of carbon nanotubes*, H. Scudder, G. Lu, and N. Kioussis *Phys. Rev. B* **68**, 205416 (2003).
14. *A nonplanar Peierls-Nabarro model and its applications to dislocation cross slip*, G. Lu, V. Bulatov, and N. Kioussis, *Phil. Mag. A* **83**, 3539 (2003).
15. *On stress assisted dislocation constriction and cross-slip (Invited article)*, Owen Richmond Memorial Special Issue), G. Lu, V. Bulatov, and N. Kioussis, *Intern. Journ. of Plasticity* **20/3**, 447-458 (2004).
16. *Correlation Effects and Materials Properties*, Vol. 2, eds. A. Gonis, N. Kioussis, and M. Ciftan, (Kluwer Academic/Plenum, New York, 2002).
17. *Dislocation core properties of Al-Cu Alloys*, A. Coho and N. Kioussis, manuscript under preparation.
18. *Ab initio studies of water monomer adsorption on the (001) Ni₃Al surface*, M. Tovar and N. Kioussis, manuscript under preparation.

V. INVITED TALKS

1. *VII International Conference on Advanced Materials – ICAM 2001*, Cancun, Mexico, August 2001.
2. *CECAM/SIMU Multiscale Modeling Workshop of Materials: Methods, Algorithms and Unresolved Problems*, Crete, Greece, June 2001.
3. *Sixth Hellenic National Congress of Mechanics*, Thessaloniki, Greece, July 2001.
4. *First International Workshop on Surface, Interface, and Thin Films*, Shanghai, China, May 2001.
5. *Alcoa Technical Research Center*, Alcoa Center, Pennsylvania, June 2001.
6. *Lawrence Livermore National Laboratory*, Division of Chemistry and Materials, April 2001.

7. *Mardi Gras Conference on Multiscale Simulation, Theoretical and Experimental Approaches to Deformation, Friction, Fatigue and Fracture*, Louisiana State University, Baton Rouge, February 2001.
8. *Electronic Structure of Complex Materials*, Georgetow University, Washington D.C., August 2002.
9. *First International Conference on Multiscale Modeling*, London, United Kingdom, June 2002.
10. *Ninth International Symposium on Plasticity*, Plasticity 2002, Aruba, January 2002.
11. *Structural and Optical properties in KDP Crystals*, Simulations of Complex Materials, March Meeting of APS, Austin, Texas, March 3-7, 2003.
12. *Linking ab initio and continuum approaches for multiscale modeling*, 5th Euromech Solid Mechanics Conference, Thessaloniki, Greece, August 17-22 2003.
13. *Bridging Length Scales and Computational Nanomechanics*, 13th International Conference on the Strength of Materials, Budapest, Hungary, 25-30 August 2003.
14. *Tuning the magnetism of strongly correlated Kondo nanoclusters*, NATO Advanced Research Workshop on "Physics of Spin in Solids: Materials, Methods, and Applications", Baku, Azerbaijan, 15-19 2003.